IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s):	Edward W. MERRILL *et al.*	Confirmation No.: 7398
Serial No.:	10/197,209	Examiner: Susan W. Berman
Filing Date:	July 18, 2002	Group Art Unit: 1711
Title:	RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PROSTHETIC DEVICES	

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS

PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34 , Example 1).

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7. Also, prior to January 20, 1995, we conducted a thermal analysis of the irradiated UHMWPE specimens, as described in paragraph 9, by use of DSC. This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity.

Six polymer samples, as described in paragraph 9, also were irradiated in sealed pans for crystallinity analysis. The samples were heated to melt and irradiated while in a molten state. A copy of Premnath Venugopalan's laboratory note book page numbers 8-9 is attached as Exhibit 3 (see Expt 1 and Expt 2). Thus, prior to January 20, 1995, we have practiced the process of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state. The DSC testing on the polyethylene samples that were irradiated in a molten state was conducted. Crystallinity levels had dropped to 37.77% (printed as 37.8%) for the sample given a 20 Mrad radiation dose. Copies of the corresponding DSC data sheets are attached as Exhibit 4 (marked as 'data-6'). Crystallinity data from unirradiated GUR415 bar stock was used as control. Irradiation dose (20 Mrad), temperature (125.51, printed as 125.5) and crystallinity data (37.77%, printed as 37.8%) from this work are presented in a patent application that became the '400 patent (see, for example, Table 1 on column 9 of the '400 patent), in the '313 application (see, for example, Table 1, page 27), and the '638 application (see, for example, Table 1, page 35).

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ESR results indicated no detectable free radicals in melt-irradiated polyethylene, whereas the control polyethylene that was irradiated at room temperature without concurrent or subsequent melting showed the presence of free radicals. The absence of free radicals in the melt-irradiated polyethylene indicates that any further oxidative degradation would be avoided, and thus the material was suitable for use in medical prostheses. See Exhibit 5 for ESR spectra from an experiment conducted prior to January 20, 1995. The ESR spectra show samples irradiated at room temperature contain free radicals; whereas, the samples irradiated at 175°C do not have any detectable free radicals.

Swell Ratios indicated that the melt-irradiated polyethylene was highly crosslinked and did not allow dissolution of polymeric chains, while unirradiated polyethylene dissolved completely, which signifies lack of cross-linking in the unirradiated polyethylene. See Exhibit 6 for swell test results of an experiment conducted prior to January 20, 1995. Swell test data shows control specimens dissolve completely within 24 hours in Decalin™ at 150°C.

9. The above testing confirmed that we had invented, among other things, (1) methods of making an improved prostheses by combining melting and irradiating to cross-link UHMWPE, and (2) improved prostheses that were the result of these processes. These prostheses are wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

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10. Prior to January 20, 1995, we also developed another embodiment to preserve the highly disordered entangled state of the UHMWPE in order to solve the wear problem (see item b of Exhibit 1). The embodiment involved cross-linking the polyethylene in at room temperature ('cold irradiation') by irradiation and subsequent melting. The process is referred to as Cold-irradiation and Subsequent Melting or "CISM " and is disclosed in U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 39, Example 8), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 47-48 , Example 8).

11. According to this embodiment, UHMWPE is irradiated at room temperature to cross-link and subsequently the irradiated UHMWPE is heated above the melting point of about 135°C and then cooled. This process subsequently referred to as cold irradiation and subsequent melting or "CISM", meaning irradiation of UHMWPE at about room temperature and then heating the irradiated UHMWPE above the melting point and resolidifying.

12. Prior to January 20, 1995, we had a number of UHMWPE specimens irradiated at room temperature at Mr. Kenneth Wright's laboratory. A copy of Mr. Wright's laboratory logbook pages number 120-121 containing a log of irradiation work done prior to January 20, 1995 is attached as Exhibit 2. The experiment (Marked as Irradiation Experiment 1) and the process including radiation doses used are recorded in lab note book no. 2, page no. 8. A copy of the laboratory note book page number 8, which is attached as Exhibit 3.

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The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

April 14, 2004	Edward W. Merrill
Date	Edward W. Merrill
Date	William H. Harris
Date	Premnath Venugopalan
Date	Murali Jasty
Date	Charles R. Bragdon
Date	Daniel O. O'Connor

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Date	Edward W. Merrill
4/22/04 Date	W Harris William H. Harris
Date	Premnath Venugopalan
Date	Murali Jasty
Date	Charles R. Bragdon
Date	Daniel O. O'Connor

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We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date	Edward W. Merrill
Date	William H. Harris
3-5-04 (3 May 04) Date	Premnath Venugopalan
Date	Murali Jasty
Date	Charles R. Bragdon
Date	Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s):	Edward W. MERRILL *et al.*	Confirmation No.: 7398
Serial No.:	10/197,209	Examiner: Susan W. Berman
Filing Date:	July 18, 2002	Group Art Unit: 1711
Title:	RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PROSTHETIC DEVICES	

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date. All dates on the attached Exhibits have been masked out.

2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,209 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same. The application also relates to processes of preparing prosthetic bearing comprising the steps of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state.

3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out

inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

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Date	Edward W. Merrill
Date	William H. Harris
Date	Premnath Venugopalan
4/22/04 Date	M urali Jasty Murali Jasty
4/21/04 Date	Charles R Bragdon Charles R. Bragdon
Date	Daniel O. O'Connor

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0063

Applicant(s):	Edward W. MERRILL *et al.*	Confirmation No.:	7398
Serial No.:	10/197,209	Examiner:	Susan W. Berman
Filing Date:	July 18, 2002	Group Art Unit:	1711
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14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false

statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date	Edward W. Merrill
Date	William H. Harris
Date	Premnath Venugopalan
Date	Murali Jasty
Date	Charles R. Bragdon
5/19/04 Date	Daniel O. O'Connor

EXHIBIT - 1

BULK CROSS-LINKING FOR IMPROVED UPE PROPERTIES
starting

BASIC MOTIVATION :-

It is clear ~~that~~ as mol. wt. of PE increases, it's abrasion resistance increases. Further as hypothesized by Prof. Merrill, the increase in entanglements should reduce wear. ~~[illegible]~~ Both ways there seems to be an effort at increasing the resistance of PE chains to ~~[illegible]~~ being pulled out of the bulk.

Hence, the following treatments ~~[illegible]~~ are being considered as ways to increase the resistance faced by PE chains against being pulled out :

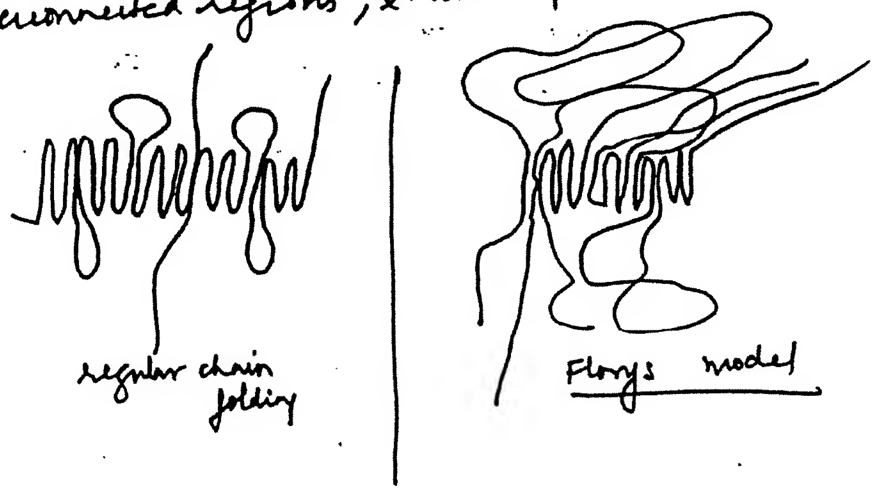
(a) Heat and rapid cooling: Heat the polymer to a completely disordered ~~state~~, highly entangled state ~~[illegible]~~ and then suddenly cool it in order to trap it in that state.

This may be possible with 10µ thick films dipped into liqd. N_2 but is not possible for larger specimens (Researchers have used several 100 to 100,000 °c/min). Further there are problems of differential crystallization at different positions and problem of stress concentrations.

(b) Crosslink as solid, melt, recrystallize: Irradiating the polymer as a solid will mean less crosslinking ~~crystallization~~ at the crystalline zones but higher crosslinking in the amorphous zones (more mobile chains can ~~[illegible]~~ jump more to connect at different places). Melting & recrystallizing these will probably again lead to the original crystal structure ~~[illegible]~~ (though with reduced crystallinity) ~~though~~ and selective segregation of crosslinks into the amorphous regions. This is expected to be more wear resistant since molecules in the tie regions may be interconnected & crosslinked. Promises to be useful if (a) inter crystalline region slip is

important during wear (~~b~~) if loss in hardness is not crucial.

(c) <u>Crosslink as melt, recrystallize</u>: More reduction in crystallinity expected with uniform crosslinking (much more than in X-linking of the solid). More likely that chain-folding in the Flory sense will occur, where ~~chains do~~ ~~not fold so~~ Instead of one chain folding repeatedly, ~~because~~ many chains will fold in a given region. Hence ~~the~~ the amorphous region will have more interconnected regions, X-link points & longer loops.



(d) <u>Crosslink the solid</u>:
~~The~~ Hardness of original UPE is retained and hopefully there will be ~~more~~ ~~etc~~ selective crosslinking in the amorphous regions.

Questions/Concerns :

① Degradation vs. Crosslinking

Degradation → Mol wt ↓
Xstallinity ↑
Wear ↑
free radicals
(long term existence)

Crosslinking → Extent ?

② Crosslinking vs. Crystallinity

Crystallinity → decreases as xlinking ↑ (if recrystallized)

③ Crosslinking vs. Crystal structure

Ideas :

① Crosslinking by irradiation of Hylamer after it has been processed and no recrystallization. ⇒ Highest crystallinity + Crosslinking.

③ Study crosslinking in HDPE instead to see extent of crosslinking, degradation etc.

IRRADIATED SPECIMENS FROM ZIMMER

* $1\,\mathrm{M\,Rad} = 10^4\,\mathrm{Gy} = 10^{8}\,\frac{\mathrm{erg}}{\mathrm{g}}$

$10^{-7}\,\cancel{\mathrm{erg}}\,\mathrm{J} = \mathrm{Erg}$

$10^{-2}\,\mathrm{Gy} = \mathrm{rad}$

$\downarrow$

$\mathrm{J/kg}$

$100\,\mathrm{rad} =$

$1\,\mathrm{Gray} = 1\,\mathrm{J/kg} = \frac{10^{+7}\,\mathrm{erg}}{10^{3}\,\mathrm{g}}$

Data 2

DSC RESULTS: Effect of freezer-milling and Effect of crosslinking by irradiation

Sample	T_{m1} (°C)	T_c (°C)	T_{m2} (°C)	% Cryst 1	% Cryst. 2	Difference in Crystallinity	Avg. Lamellar thickness 1	Avg. lamellar thickness 2
(3A) GUR 415 – CONTROL	135.83	122.80	127.52	62.91	46.42	16.49	2.91×10^{-6}	1.51×10^{-6}
(MJ1) GUR 415 – FREEZER-MILLED – 10 Min.	121.86	154.11	104.47	0.28 So low a crystallinity?	0.57 Again low even after heating?	−0.30	1.15×10^{-6}	0.653×10^{-6}
BAR – CONTROL	127.39	121.71	126.57	52.92	46.37	6.55	1.52×10^{-6}	1.44×10^{-6}
				Nearly constant		Increasing	Increasing	Decreased, if constant
BAR – 10 MRad	130.53	127.95	119.05	54.02	45.29	8.73	1.84×10^{-6}	1.02×10^{-6}
BAR – 20 MRad	131.05	129.48	119.78	54.95	41.69	13.26	2.05×10^{-6}	1.05×10^{-6}

EXHIBIT - 2

1.45

COOP COMPUTATION BOOK

NAME	NUMBER
KEN WRIGHT	1

Course F-13 a.m.

Used from to

HARVARD COOPERATIVE SOCIETY
1400 MASS. AVE., CAMBRIDGE, MASS. 02138

TECH. COOP
84 MASS. AVE. CAMBRIDGE, MASS. 02139

	Merrill	10	2.5	41	15	1.1	75	1.3	$1.25 \times 10^{?}$
	Bertrand	1-2	2.5	39,	–	–	90	–	1.25×10^{6} 11
PEO collagen / Collagen on millipore filter	Perez	1-9 } 1-6 }	2.5	62	24.	1.1	430	1.3	2×10^{6}
(750 Liters Liquid N_2)									
PMMA ~4" dia discs ½" thick	Earl Williams	1	2.5	20	8.1	1.1	40	3.2	2.5×10^{5}
		2	–	26	10.2	–	–	–	3×10^{5}
		3-5	–	26	–	–	–	–	–
		6-8	–	–	–	–	–	–	–
		9-10	–	17	6.8	–	58	–	2.5×10^{5}
3/8" thick		11	2.0	33	10.2	–	90	–	3×10^{5}
		12-15	–	39	11.9	–	90	–	3.5×10^{5}
1-3 Goretex / 4- 9 chs of PEO's different concentration	Schmitt	1-18	2.5	39	15.	1.1	400	1.3	1.25×10^{6}
		1-13	–	–			–	–	$~~1.25~~ \times 10^{6}$
		2-8	–				200		5×10^{6} 11
Thin Films Polyurethane	Mimser Moslehi 3-2108, Rm 35-332	1-3	–	30	12	–	100	1.3	10^{6}
		4-6	–	–	–	–		–	1.25×10^{6} 111
Small (~0.5 cm dia) cups	Premnath Venugopalan	1-6	2.5	39	15	1.1	75	1.3	1.25×10^{6}
		2-6	–				–		–
		3-6	–	–		–	–	–	– 11
		4-6	–	52	20		–	–	– 111
		5-6	–	63	24		–	–	2×10^{6} ~~1111~~
		6	–			–	"		" ~~1111~~
		–	–	–	–	–	–	–	~~1111~~
		6	–	–	–	–	–	–	– ~~1111~~
Slush	Tufts MB Med Center	1-4	2.5	33	13.6	–	430	1.5	10^{6} 11
		–	–	–	–	–	–	–	11
		5-8	–	–	–	–	–	–	– 11
		–	–	–	–	–	–	–	– 11
		9-12	–	68	27.	–	–	–	2×10^{6}
		–	–	–	–	–	–	–	–
Various strips Goretex	Schmitt	1-6	–	38	15.	–	125	–	1.25×10^{6}
		1-6	–	–	–	–	–	–	–
		~~1-4~~	–	–	–	–	–	–	11
		1-3 ~~[illegible]~~	–	–	–	–	–	–	–

No overlay (sufficient liquid overlay)

$\leq 2.5\times10^6$

Glass cover overlays

$\leq$ Pb over central area

No Pb.

2 overlays

$\leq 2.5\times10^6$ #Hummed over

$\leq 5\times10^6$

$\leq$

$\leq 2.5\times10^6$

$\leq 5\times10^6$

$\leq 10^7$

$\leq 2\times10^7$

$\leq 3\times10^7$

$\leq 4\times10^7$

$\leq 5\times10^7$

$.5\times10^6$ 2 overlays

$\leq 5\times10^6$ (.stone may be slightly less than 5×10^6)

~~#4 n 2-5 x10~~

$1-3 \rightarrow 5\times10^6$

Polyethylene + Acetone, naphthalene, water	Schmitt	1-2	2.6	50	20	1.1		1.5	1.55×10^6
PEO in Petri dishes	Stephanie Lopina, Prof. Cima	1-10	2.6	30	12	1.1	2.50	1.3	10^6 //
	Stephanie Lopina 3-7115 354-7489	1-15	—	60	24	—	340	—	2×10^6
		1-20	—	—	—	—	440	—	—
Book — wetted + dried	Chet Cooke	1	2.6	60	24	1.1	160	1.3	2×10^6
		2	—	—	—	—	—	—	—
		3,4	—	—	—	—	200	—	— //
PMMA 6×6" (1-16) (Fractal) 17-32, Cubes + other shapes	Ken Brecher B.U. Dept of Astronomy 725 Comm. Ave 02215 353-2625	1-6	2.1	186	6.8	1.0	140	3.2	2×10^5
		7-12	—	17.5	6.0	—	—		
		13-32					180		
		33-42					180		
		—							
		—		85					
PTFE + Polyethylene PEO*		1-3	"	37	18	1.1	140	1.3	1.25×10^6
PEO in Petri Dishes see above		1-20	"	30	12.	1.1	440	1.3	10^6 //
	Prof Cima	1-15	—	60	24	—	360	—	2×10^6
Polyethylene oven — hot plate	Premnath Venugopalan	1-4	2.8	70	30.	.	85	—	2.5×10^6
		1-3	—	—	—	—	—	—	— //
		1-2	—	—	—	—	—	—	— ///
		1	—	—		—	—	—	~~////~~ /
			—	—		—		—	~~////~~ /
See above	Stephanie Lopina	1-15	2.6	30	12	1.1	355	1.3	10^6
Polyethylene 1-4 hot plate	Premnath Venugopalan	1-8	2.6	37.5	15	—	135	1.3	1.25×10^6
		1-3,5-7	"	52				—	1.83×10^6 ////
		1-2,5-6	2.8+	52	24	—	105	—	2×10^6 ~~////~~
		1,5	—	—		—	—	—	— ////
		"	—	—		—	—	—	— ~~////~~ ////
PEO Soln PTFE° Polyethylene * small beads*	Schmitt Premnath 1-6*	1-2°, 1-4,1-6°	2.6	37.5	15	—	165	1.3	1.25×10^6
		1-4,1-5*, 1-2°		—	—	—	—	—	—
		1-4, 1-4*		—	—	—	—	—	—
		1-3, 1-4*		—	—	—	—	—	—
		1-3, 1-3*	2.75	47	20	—	—	—	1.06×10^6
		1-2, 1-2*		—	—	—	—	—	—
		1, 1*		—	24	—	100	—	1.25×10^6

1 8 C L N i

2 curdays

$\Sigma 2\times10^6$

Turned over for 2nd run

1 discharged

Petri dishes $\bar{c}$ glass cover

$\Sigma 2\times10^6$

$\Sigma 10^7$
$\Sigma 2\times10^7$
$\Sigma 3.5\times10^7$
$\Sigma 5\times10^7$

$\Sigma 2\times10^6$

$\Sigma 20$ 1st run hot plate jammed before irradiation - adjusted and passed through
$\Sigma 9.8\times10^6$
$\Sigma 19.8\times10^6$
$\Sigma 29.8\times10^6$
$\Sigma 49.8\times10^6$

$\Sigma 2.5\times10^6$
$\Sigma 3.75\times10^6$
$\Sigma 5\times10^6$
$\Sigma 10^7$
$\Sigma 2\times10^6$
$\Sigma 5\times10^7$

EXHIBIT - 3

Student's Name **Date**

Subject **Instructor's Name**

Irradiation Studies.

e^- beam at HVRL, MIT.

✓Kenneth. A. Wright.

Student's Name Date

Subject Instructor's Name

EXPT [1 → Irradiation of solid polymer (UPE) from barstock]

Irrad/RT/AW/NO FUHT ~~PANS~~

Set 1

12 samples of thickness of a few microns kept between two slides

RT
- 1.0 MRad (2 each)
- 2.5 MRad
- 5.0 MRad
- 10.0 MRad
- 20 MRad
- 50 MRad

This was for studies under polarizing microscope at MGH

Result → all showed ... spherulites on melting & cooling under microscope

Set 2

6 samples in DSC pans

RT
- 1.0 MRad
- 2.~~77~~ "
- 5.0 "
- 10.0 "
- 20.0 "
- 50.0 "

DSC Runs done & results in the file (#3)

Student's Name   Date

Subject   Instructor's Name

EXPT. (2) Irradiation of barstock while a melt.

Irrad/175C/Air/No follow H.T./RAMS → FUHT

6 Samples → 1.0, 2.5, 5, 10, 20, 50 MRads.
at temp. >150°C
Range (155 to 180°C approx.)

Heating → Sample heated ~~approx. once~~ intermittently.

Heated → 1.0 MRad → Heated → 2.5 MRad → heated → 5.0 MRad → Heated → 10 MRad → Heated → 20 MRad → Heated → 35 MRad → Heated → 50 MRad

Samples placed on a heated Al plate (sink).

Analysis → In file #3.

DSC trivia:

Dose	mg
1	9.732
2.5	11.433
5	9.540
10	9.061
20	10.133
50	11.638

There was some confusion because the heating erased ~~damaged~~ the marks on the pans. Weights were correlated by measuring again. Fortunately, the weights were well distributed and each adequately far apart from another.

Student's Name Date

Subject Instructor's Name

EXPT. 3 : Irrad. / 175 C / N_2 atm / NO follow-up HT / VIALS

→ FUHT

Samples :- Barstock (from surface) → constant radius.
Samples b/ws 2.5 to 3cm radii

4 Samples → 2.5, 10, 20, 50 MRad

Method :- Thin strips in vials.

Vial filled with N_2 as in heat treatments.

Heater used this was small enough to fit under generator outlet

(heater provided by Prof Merrill)

cooling in air (Room temp.)

Sample left in vial with N_2 atmosphere at RT after irrad. for >5 days

Analysis

Student's Name

Subject Instructor's Name

EXPT 4: Irrad/175C/~~Air~~/NO FUHT/VIAL

Samples: Bar stock (b/w 2.5 to 3 cm radial distance)

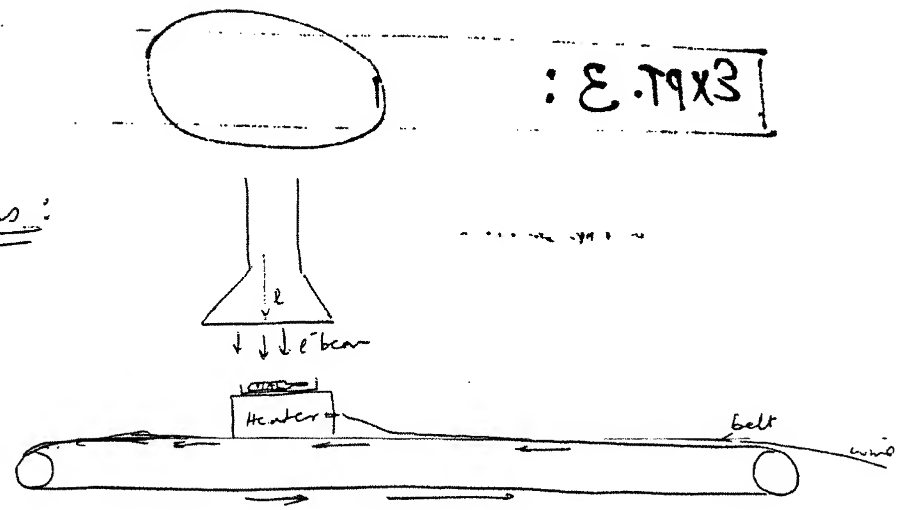
4 Samples → 2.5, ~~10~~ (9.8), ~~20~~ (19.8), 50 M Rad.

Method: (As on previous page)

Analysis

EXPT. 3 :

Apparatus :



Student's Name

Dat

Subject

Instructor's Nam

EXPT 5 : Irrad / RT / N_2 / NO-FUHT / VIAL

Samples → Same as last page.

Method → Same as last page.

	Dose	
1	2.5	MRad
2	9.8	"
3	19.8	"
4	50	"

EXHIBIT - 4

E-IRRADIATION OF
THE MELT.

E-IRRADIATION OF THE MELT

Procedural Details:

The following experiment was performed at HVRL, MIT. The Points to be noted ~~Dep~~ were as follows:

(1) Since the hot plate would not fit under the Van de Graaf generator, the specimens in DSC pans were placed in between two petridishes and laid on a metal plate acting as a heat sink while heating (supplies heat when placed on the belt).

(2) The heating was done at intervals ~~between~~ at .....

- Start
- After 1.0 MRad
- " 2.5 MRad
- " 5.0 MRad
- " 10.0 MRad
- " 20.0 MRad
- " 30.0 MRad
- After 40.0 MRad

(3) It can be assumed that approximately the temperature of the specimens was between 150 – 200 °C

NOTE:

① Absence of bimodal distribution during crystallization
→ because no crystals during irradiation,
One phase.
(Scission & x-linking .. different in crystalline regions)

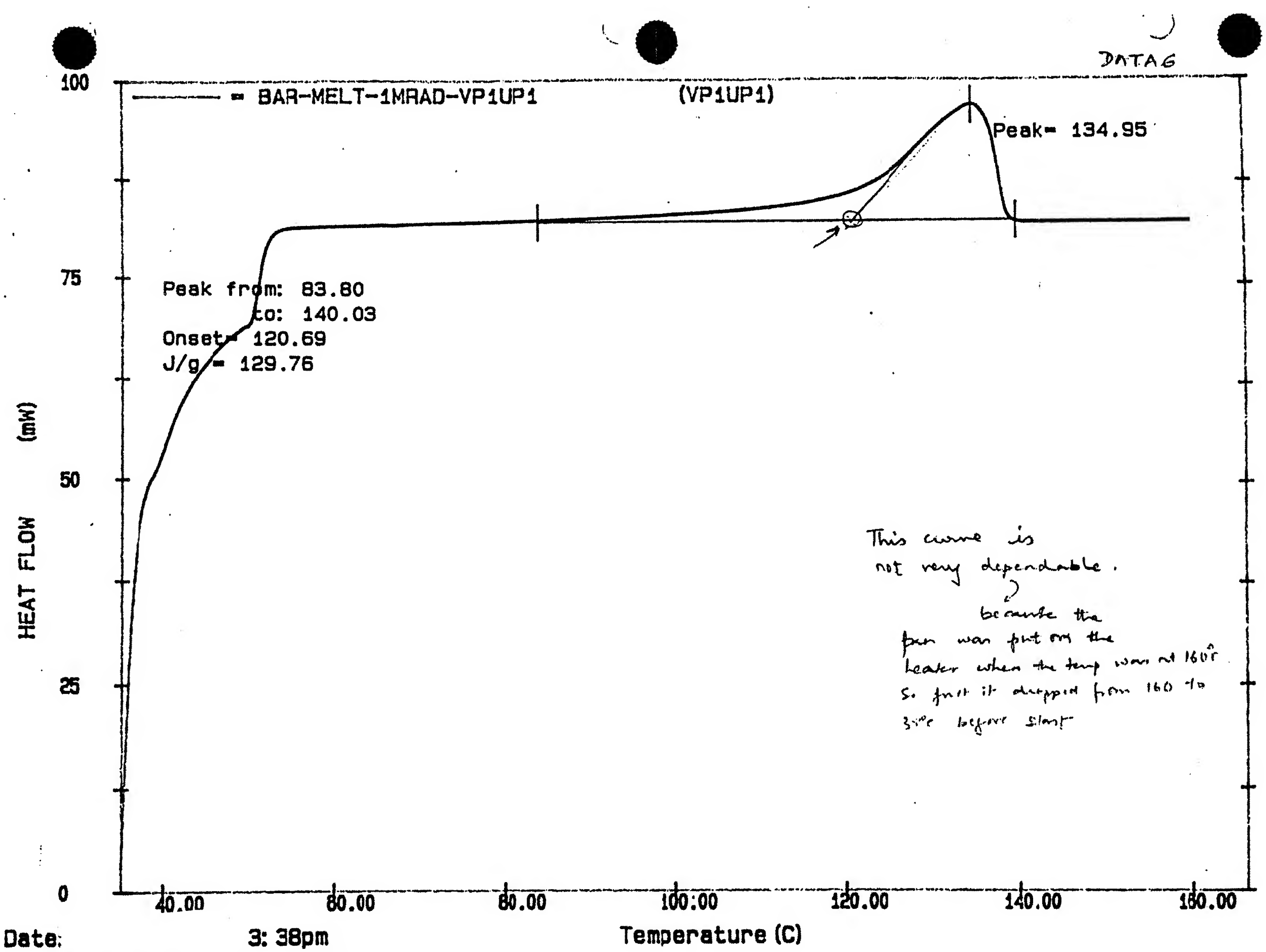
② Since lamellar size and crystallinity & Tm decreases,
→ (crystal size)
significant crosslinking occurring in proportion to scission.
If too much scission compared to crosslinking
⇒ mol wt would decrease
⇒ crystallinity & crystal size will increase
(eg) HDPE → 60%.

Data 6

NRad	T_{m1} (°C)	[illegible]	% Cryst. 1	Avg. lamellar thickness ($\times 10^{-6}$)	T_c	T_{peak}	T_{m2}	T_{peak2}	% Cryst. 2	Avg. lamellar thickness ($\times 10^{-6}$)	Cryst. diff.	Remark.
1	120.69	[illegible]	44.87	1.10	123.93	120.27	120.60	[illegible]	48.20	1.08	-3.38	
2.5	120.81	[illegible]	46.15	1.11	122.93	118.51	119.73	[illegible]	48.41	1.05	-2.26	
5	121.97	[illegible]	43.29	1.16	121.14	117.96	120.20	[illegible]	45.18	1.07	-1.90	
10	120.49	[illegible]	40.33	1.09	118.95	113.68	118.73	[illegible]	37.77	1.01	2.56	
20	118.16	[illegible]	37.77	0.995	115.06	111.15	117.37	[illegible]	39.09	0.957	-1.31	No second valley during xstallizing
50	109.84	[illegible]	31.64	0.759	105.50	101.18	109.65	[illegible]	32.77	0.748	-1.11	No second valley during xstallizing
	Suddenly drop	decr.	decr.	decr.	decr.	decr.	decr	decr.	decr.			

Note:
① Crystallinity is down below 40% for the first time.
② Sudden drop in T_{m1} (as in irrad. of solid PE) after 20 MRad. (Both T_{m1} & T_{m2})
③ T_{peak} consistent but decreasing as rad. dose increased (Both T_{peak}, & T_{peak2})
④ Original Bar cryst → 55%
Irrad. melt & solidify → 30-45%

T_{m1} decrease corresponds to Mw decrease.



Date: 3: 38pm
Scanning Rate: 10.0 C/min
Sample Wt: 9.732 mg Path: C: \PE\
File 1: VP1UP1 *PREMI*

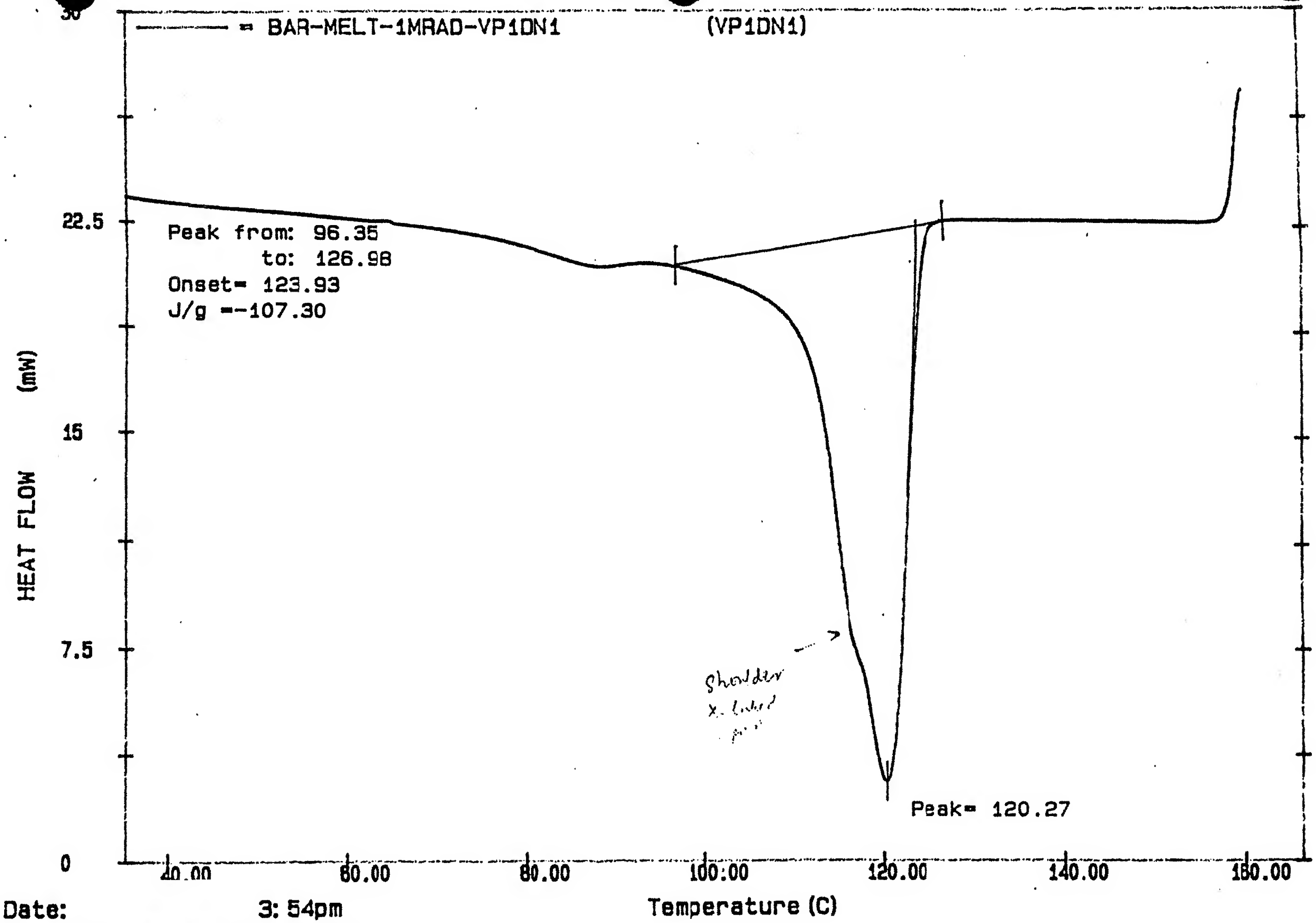
PERKIN-ELMER DSC7

MISCELLANEOUS DSC SAMPLES

SAMPLE NAME	Tm onset 1 C°	Tm (K^) onset 1	To (C) onset	To (K) onset	Tm onset (C)2	Tm (K) onset 2	ΔHm 1 (J/gm)	ΔHm 1 (Cal/gm)	ΔHe (J/gm)	ΔHe (Cal/gm)	ΔHm 2 (J/gm)	ΔHm 2 (Cal/gm)	%Cryst 1	%Cryst 2	Ave Lamellar Thickness 1	hhw (C°)1	Ave Lamellar Thickness 2	hhw (C°) 2	Peaks M1	Peaks O1
GUR 415 POWDER	133.81	416.96	119.79	392.94	124.85	398.00	172.88	41.27	127.22	30.41	132.58	31.69	59.44	45.79	2.39E-08	7.12	1.31E-08	6.68	142.87	115.51
GUR 415 PWDR ETCHED 10 MIN	132.80	415.95	119.61	392.76	124.16	397.31	197.95	47.31	109.01	26.05	116.01	27.73	68.37	40.07	2.19E-08	8.12	1.27E-08	5.77	141.25	115.61
HERCULES 1900 POWDER	133.41	416.56	119.27	392.42	125.03	398.18	224.29	53.61	129.38	30.92	125.03	29.88	77.47	43.18	2.30E-08	6.16	1.32E-08	6.76	142.18	114.51
HERCULES 1900 POWDER HEAT TREATED 145C-10 DAYS	122.21	395.36	115.90	389.05	122.73	395.88	137.06	32.76	120.70	28.85	136.37	32.59	47.34	47.10	1.17E-08	8.34	1.19E-08	9.07	131.45	112.25
POLYETHYLENE FIBERS	144.19	417.34	121.39	394.54	125.09	398.24	211.73	50.60	139.49	33.34	133.29	31.86	73.13	46.04	3.30E-05	4.10	1.33E-08	6.77	146.80	115.45
HERC. 1900 175C-5DAYS UNETCHED	119.62	392.77	116.51	389.66	120.07	393.22	133.15	31.82	108.35	25.90	134.12	32.06	46.19	46.32	1.05E-08		1.09E-08		129.40	113.88
HERC. 1900 125C+200C 5DAYS EA. NORM	133.25	416.40	116.51	389.66	121.42	394.57	158.68	37.93	119.68	28.60	156.21	37.34	54.81	53.95	2.27E-08		1.12E-08		130.46	114.82
HERC. 1900 ETCHED 10 MIN.	133.90	417.05	119.53	392.68	125.24	398.39	206.30	49.31	123.56	29.53	132.07	31.71	71.25	45.62	2.41E-08	5.18	1.34E-08	5.79	141.43	115.86
HERC. 1900 145C-10DAYS ETCH.10 MIN.	122.16	395.31	116.26	389.41	123.07	396.22	134.14	32.06	115.38	27.58	131.04	31.32	46.33	45.28	1.17E-08	9.10	1.21E-08	9.00	132.06	112.20
HERC. 1900 125+200C-5DAYS EA. ETCHED 60 MIN.	120.58	393.73	115.42	388.57	121.71	394.86	142.28	34.01	117.19	28.01	132.08	31.56	49.14	45.61	1.08E-08	7.39	1.14E-08	7.89	128.65	113.30
HERC. 1900 125+200C-5DAYS EA. ETCHED 15 MIN.	120.69	393.84	115.46	388.61	120.24	393.39	142.44	34.04	119.85	28.64	143.82	34.37	49.10	49.67	1.10E-08	7.53	1.07E-08	7.92	128.85	113.31
HERC. 1900 175C-5DAYS ETCH. 15 MIN.	121.17	394.32	115.37	388.52	121.47	394.62	100.48	24.02	111.18	26.57	104.49	24.97	34.70	36.09	1.12E-08	8.81	1.12E-08	8.27	127.93	113.89
PE + DICHLOROBENZENE	83.32	316.47	114.81	387.96	118.14	391.29	60.14	14.37	32.21	7.70	39.25	9.38	20.77	13.56	4.33E-07		9.65E-07		95.89	112.10
HEAT TREATED CUP 1	124.57	397.72	119.17	392.32	123.51	396.66	135.48	32.38	116.92	27.94	130.90	31.29	46.79	45.21	1.31E-08	13.07	1.23E-08	11.84	133.75	115.19
HEAT TREATED CUP 2	123.71	396.86	118.87	392.02	123.20	396.35	143.74	34.35	117.28	28.03	135.14	32.30	49.65	46.68	1.25E-08	12.38	1.21E-08	10.52	133.20	115.44
CONTROL CUP	121.79	394.94	119.29	392.44	123.87	396.02	143.25	34.24	114.86	27.46	135.47	32.38	49.48	46.79	1.15E-08	13.64	1.24E-08	11.16	133.48	115.61
[redacted]																				
GUR 415 CONTROL POWDER	135.83	408.98	122.90	396.05	127.52	400.67	182.14	43.53	128.59	30.73	134.39	32.12	62.91	46.42	2.01E-08	10.02	1.61E-08	9.14	143.36	119.44
GUR 415 HEAT TREATED 5 DAYS @175C POWDER TOP	112.49	385.64	108.93	382.08	112.77	385.92	143.65	34.31	108.93	26.03	140.87	33.67	49.58	48.65	8.21E-07	16.88	8.21E-07	14.46	123.83	102.93
GUR 415 HEAT TREATED POWDER 5 DAYS @ 175C BOTTOM	116.56	389.71	116.72	389.87	117.75	390.90	145.38	34.75	135.63	32.39	142.15	33.97	50.21	49.10	9.39E-07	18.76	9.71E-07	17.60	131.79	113.08
ZIMMER CONTROL CUP UNIRRAD.	127.86	401.01	121.67	394.82	126.27	399.42	149.37	35.70	121.14	28.95	137.22	32.80	51.59	47.39	1.56E-08	12.86	1.41E-08	12.74	137.29	117.29
ZIMMER CONTROL CUP UNIRR. HEAT TREATED 5 DAYS @ 175C	107.63	380.78	121.24	394.39	114.94	388.09	125.09	29.90	134.30	32.10	129.31	30.91	43.20	44.66	7.14E-07	27.97	8.80E-07	27.27	132.00	116.81
[redacted]																				
ZIMMER CONTROL CUP UNIRR. HEAT TREATED 5 DAYS @ 175C	110.15	383.30	120.48	393.63	106.99	380.14	142.24	34.00	116.06	27.74	146.83	35.09	49.13	50.71	7.90E-07		8.96E-07		133.95	114.95
HDPE POWDER CONTROL	119.36	392.51	118.00	391.15	118.04	391.19	174.29	41.66	144.80	34.62	176.28	42.13	60.20	60.89	1.04E-08		9.01E-07		126.68	113.38
HDPE POWDER HEAT TREATED 5 DAYS @175C	122.00	395.15	115.11	388.26	118.90	392.05	189.37	45.26	143.51	34.30	186.40	44.55	65.41	64.38	1.16E-08		1.01E-08		130.02	113.09
GUR 415 POWDER HEAT TREATED 5 DAYS @ 175C HT3	118.39	391.54	115.77	388.92	117.44	390.59	131.05	31.32	114.00	27.25	152.99	36.57	45.26	52.84	1.00E-08		9.80E-07		131.05	111.88
GUR415 CUP HEAT TREATED 5 DAYS @ 175C HT3	124.52	397.67	120.06	393.21	122.81	395.96	153.27	36.63	122.16	29.20	140.99	33.70	52.94	48.70	1.30E-08		1.19E-08		134.79	115.65
GUR415 BAR STOCK CONTROL HT1	127.44	400.59	120.87	394.02	125.42	398.57	145.29	34.73	129.89	31.04	145.78	34.84	50.18	50.35	1.52E-08		1.35E-08		135.76	116.61
GUR415 BAR STOCK HEAT TREATED 5 DAYS @ 175C HT4	124.91	398.06	120.78	393.93	123.55	396.70	141.47	33.81	101.82	24.34	145.35	34.74	48.86	50.20	1.33E-08		1.23E-08		134.67	116.51
POLYSCIENCE UPE POWDER FREEZER MILLED 10 MIN	121.86	395.01	154.11	427.26	104.47	377.62	0.80	0.19	7.76	1.85	1.66	0.40	0.28	0.57	1.15E-08		6.63E-07		124.20	120.84
UNIRRADIATED GUR415 BAR STOCK CONTROL SENT W/IRRADIATED POLY	127.39	400.54	121.71	394.86	126.57	399.72	153.23	36.62	133.26	31.85	134.26	32.09	53.02	46.37	1.52E-08		1.44E-08		136.68	117.19
GUR415 BAR STOCK G IRRADIATED @10 MRAD	130.53	403.68	127.95	401.10	119.05	392.20	158.41	37.38	124.52	29.78	131.13	31.34	54.02	46.29	1.84E-08		1.02E-08		140.60	120.85
GUR415 BAR STOCK G IRRADIATED @20 MRAD	131.95	405.10	129.48	402.63	119.78	392.93	159.08	38.02	120.12	28.71	120.71	28.85	54.95	41.69	2.05E-08		1.05E-08		141.88	122.89
[redacted]																				
GUR 415 BAR STOCK E-IRRADIATED @ 1MRAD	128.13	401.28	120.38	393.53	123.42	396.57	0.00	0.00	110.70	26.46	144.01	34.42	0.00	49.74	1.58E-08		1.33E-08		131.47	113.62
GUR 415 BAR STOCK E-IRRADIATED @ 2.77MRAD	129.55	402.70	120.28	393.43	122.95	396.10	158.74	37.94	107.85	25.78	132.15	31.58	54.83	45.64	1.73E-08		1.20E-08		131.95	114.61
GUR 415 BAR STOCK E-IRRADIATED @ 5MRAD	129.98	403.13	120.47	393.62	123.09	396.24	157.62	37.67	108.15	25.85	136.59	32.65	54.44	47.18	1.76E-08		1.21E-08		131.25	115.10
GUR 415 BAR STOCK E-IRRADIATED @ 10MRAD	130.10	403.25	119.95	393.10	122.72	395.87	162.72	38.89	109.61	26.20	144.63	34.57	56.20	49.98	1.79E-08		1.19E-08		131.64	114.90
GUR 415 BAR STOCK E-IRRADIATED @ 20MRAD	128.37	401.52	118.71	391.86	117.96	391.11	158.41	37.86	111.40	26.63	120.70	28.85	54.71	41.69	1.61E-08		9.76E-07		136.59	114.76
GUR 415 BAR STOCK E-IRRADIATED @ 50MRAD	129.01	402.16	125.41	398.56	118.15	391.30	167.45	40.02	109.30	26.12	129.80	31.02	57.83	44.83	1.67E-08		9.65E-07		142.65	118.06
[redacted]																				
MELT GUR 415 BAR STOCK @ 1MRAD	120.69	393.84	123.93	397.08	120.60	393.75	129.76	31.01	107.30	25.65	139.65	33.35	44.82	48.20	1.10E-08		1.08E-08		131.95	120.27
MELT GUR 415 BAR STOCK @ 2.5MRAD	120.81	394.06	122.96	396.11	118.73	392.88	133.91	31.83	104.09	24.88	140.15	33.50	46.15	48.41	1.11E-08		1.05E-08		131.89	118.61
MELT GUR 415 BAR STOCK @ 5MRAD	121.97	395.12	121.14	394.29	120.20	393.35	125.33	29.95	123.46	29.51	130.62	31.27	43.29	45.10	1.16E-08		1.07E-08		131.11	117.96
MELT GUR 415 BAR STOCK @ 10MRAD	120.49	393.64	118.95	392.10	118.73	391.88	116.78	27.91	120.43	28.78	109.37	26.14	40.33	37.77	1.09E-08		1.01E-08		121.36	113.98
MELT GUR 415 BAR STOCK @ 20MRAD	118.16	391.31	115.06	388.21	117.37	390.52	109.37	26.14	111.45	26.64	113.17	27.05	37.77	39.09	9.85E-07		9.87E-07		121.61	111.16
MELT GUR 415 BAR STOCK @ 50MRAD	109.84	382.99	105.50	378.65	109.65	382.80	91.87	21.91	89.64	21.42	94.88	22.68	31.69	32.77	7.59E-07		7.48E-07		117.79	101.18

MISCELLANEOUS DSC SAMPLES

Peaks M2		CRYST DIFF
132.92		13.85
130.88		28.30
132.97		34.28
132.30		0.24
135.18		27.09
130.28		-0.34
129.60		0.85
132.28		25.43
133.05		1.07
128.20		3.53
128.18		-0.48
128.10		-1.38
125.35		7.22
131.45		1.57
130.92		2.97
130.80		2.89
134.09		18.45
122.55		0.93
129.38		1.12
134.91		4.20
132.83		-1.44
132.13		-1.61
127.71		-0.89
127.32		1.03
128.25		-7.51
132.80		4.24
133.79		-0.17
133.17		-1.34
117.83		-0.30
134.70		6.66
134.85		8.73
136.00		13.26
135.05		-49.74
133.15		9.16
131.98		7.26
131.18		6.25
130.30		13.02
131.10		13.00
135.95		-3.31
135.83		-2.21
132.45		-1.80
130.05		2.86
125.79		-1.31
117.85		-1.11

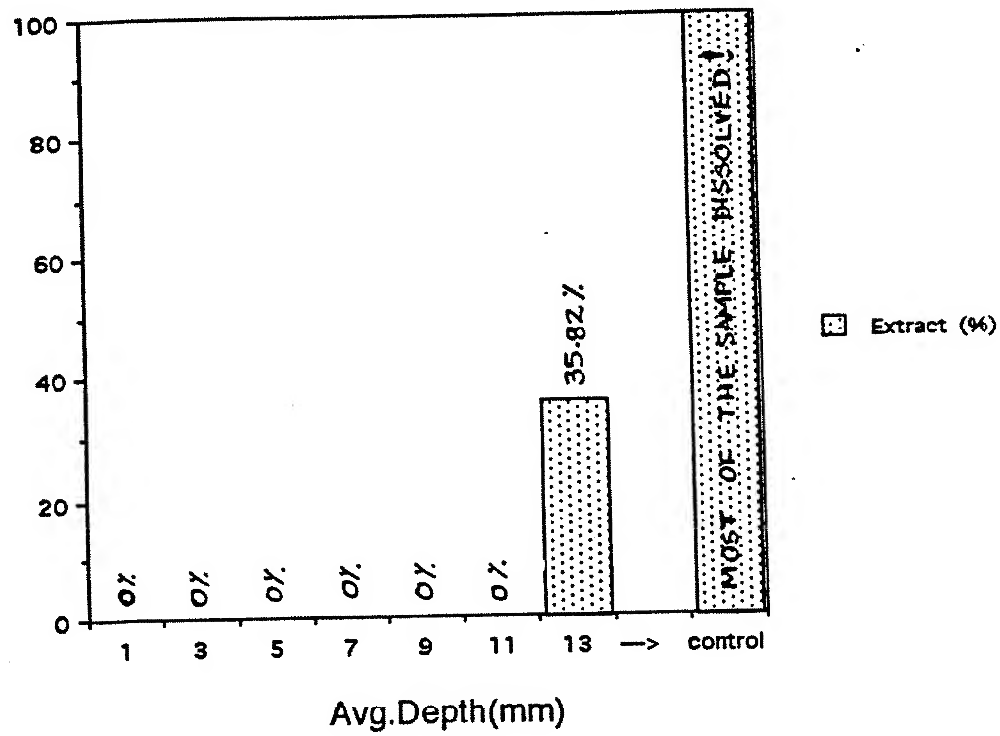


Date: 3: 54pm
Scanning Rate: -10.0 C/min
Sample Wt: 9.732 mg Path: C: \PE\
File 1: VP1DN1 PREMI

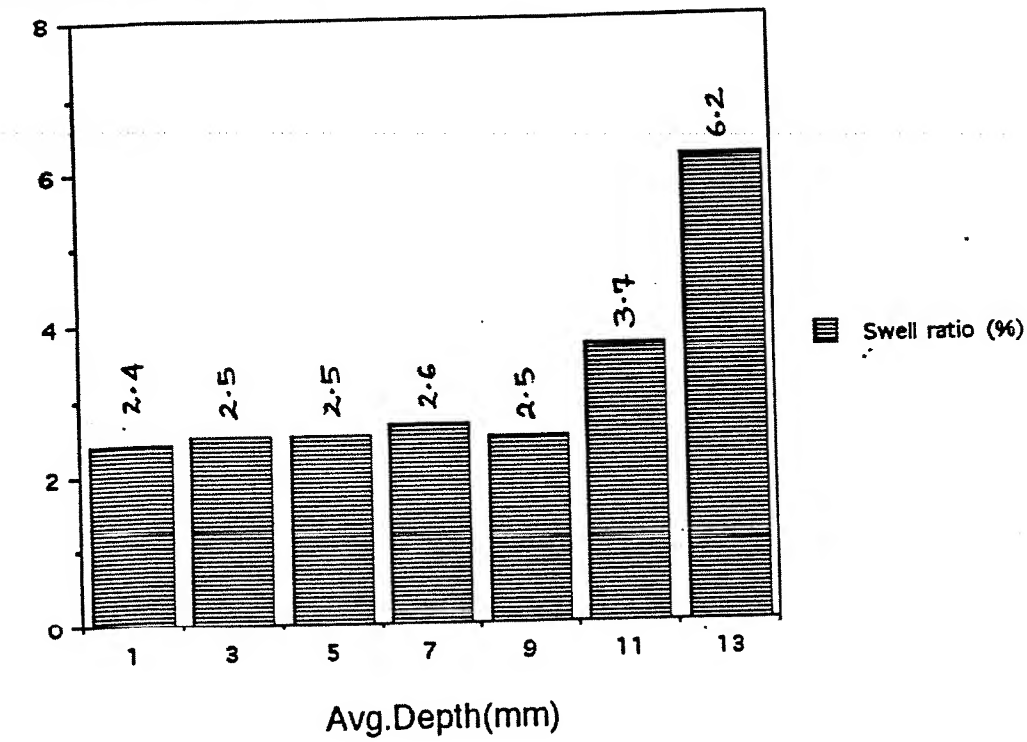
PERKIN-ELMER DSC7

EXHIBIT - 5

Extract percent in Decalin at 150 C (Samples from axis of irradaited cup 3)



Results from swelling test in Decalin at 150 C (Samples from axis of irradiated cup 3)



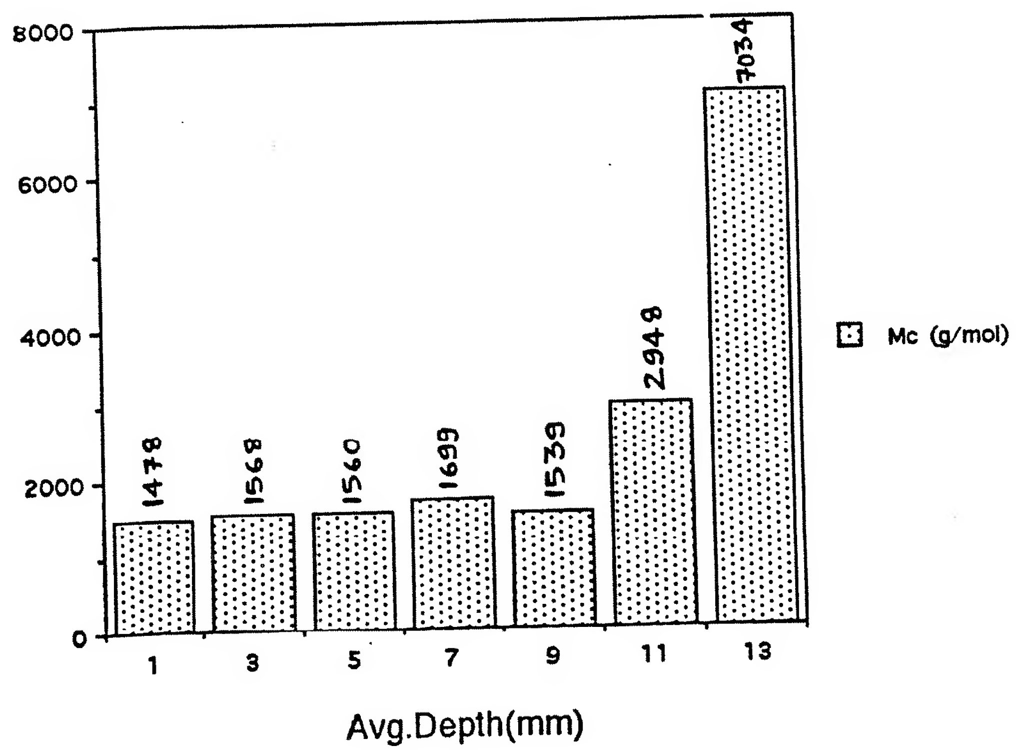


EXHIBIT - 6

EPR Data

Tony Modestino for Premnath
Operator

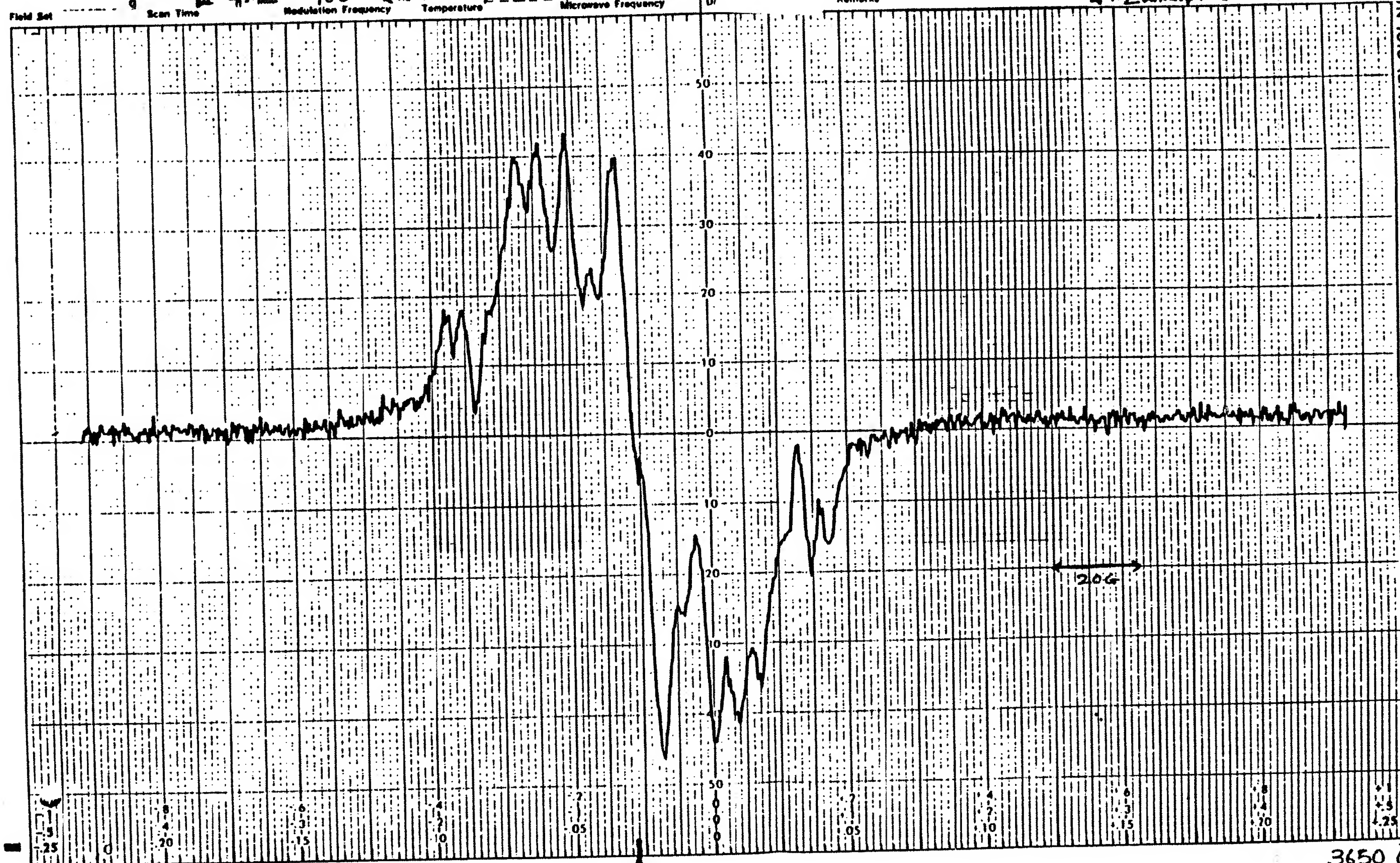
Sample: Bar Stock Irradiated as solid at RT
& N_2 atmosphere on
Remarks

RECORDING CHARTS

3350 ± 3650 G Scan Range | 1.28 msec Time Constant | 9.74 × 10^{-1} G Modulation Amplitude | 2 × 10^4 Receiver Gain | 1 mW Microwave Power

Field Set ______ G | 4 min Scan Time | 100 kHz Modulation Frequency | Room temp. ____ °C Temperature | 9.75 GHz Microwave Frequency | Dr

/N 1010 (EPR CHART A) Sample ______ Spectrum No. ______



3350 G

3480.43 G
= 19.5 G

3650 G

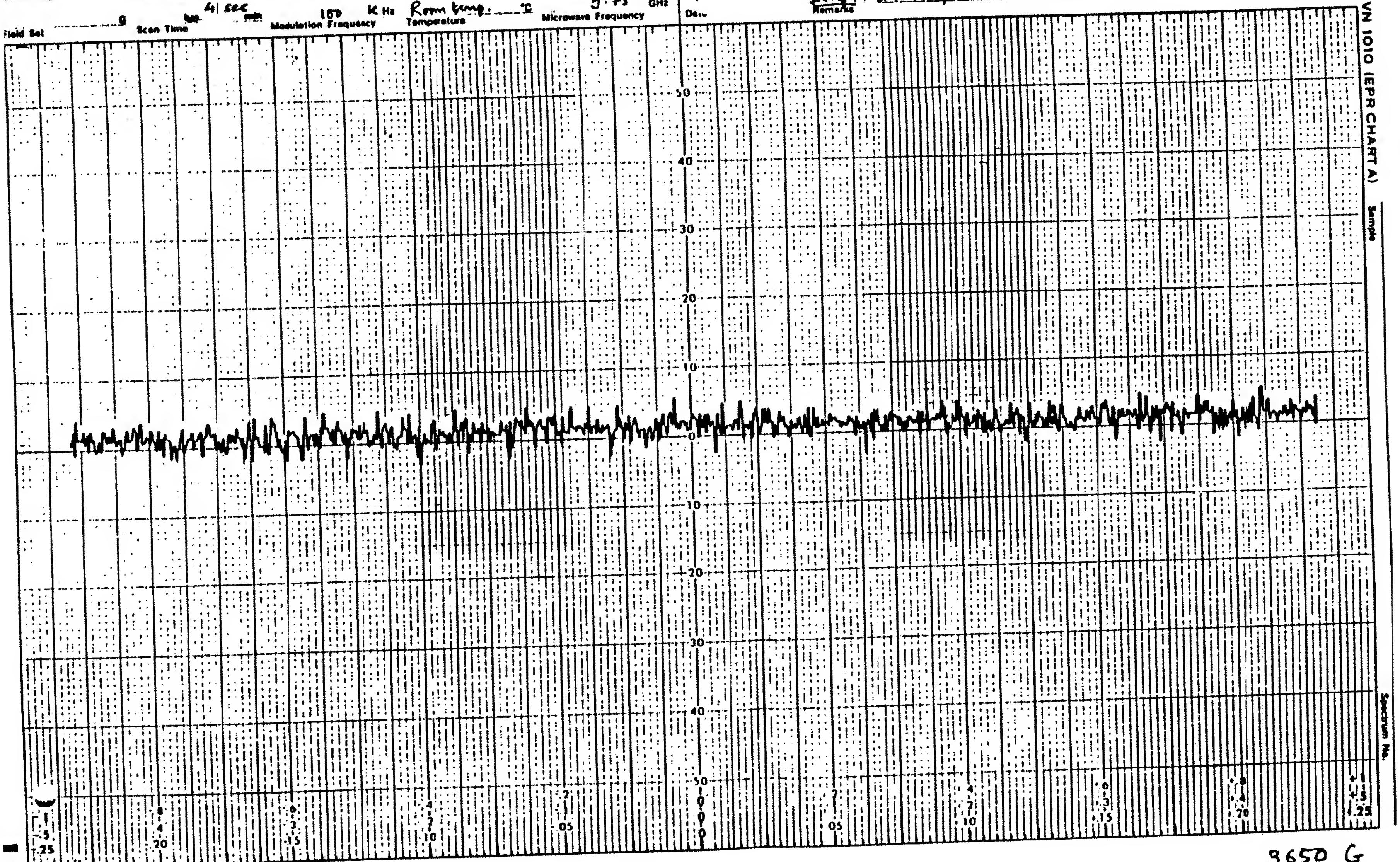
(16)

3350 ± 3650 G Scan Range | 1.28 msec Time Constant | 9.74 × 10^{-1} G Modulation Amplitude | 2 × 10^{4} Receiver Gain | Microwave Power 1 mW | Tony Modestino for Premnath Op

Field Set ______ G | 41 sec Scan Time | 100 KHz Modulation Frequency | Room temp. °C Temperature | 9.75 GHz Microwave Frequency | Date

Sample: Box Stock/melt Strand under N_2 on Remarks

VN 1010 (EPR CHART A) Sample

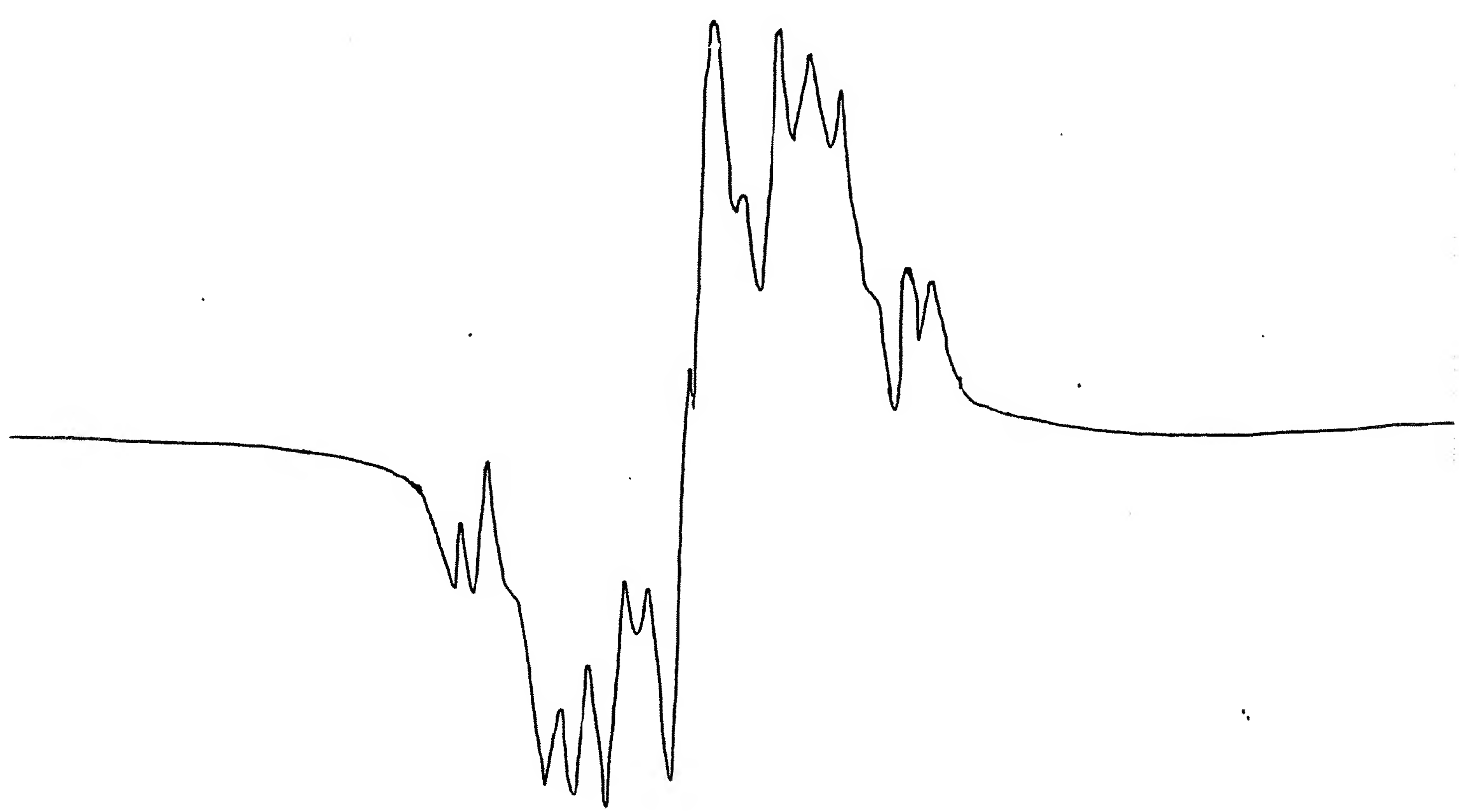


3350 G

3650 G

(17)

MIRROR IMAGE OF ESR SPECTRUM OF UHMWPE IRRADIATED AT RT / N_2 ATM.



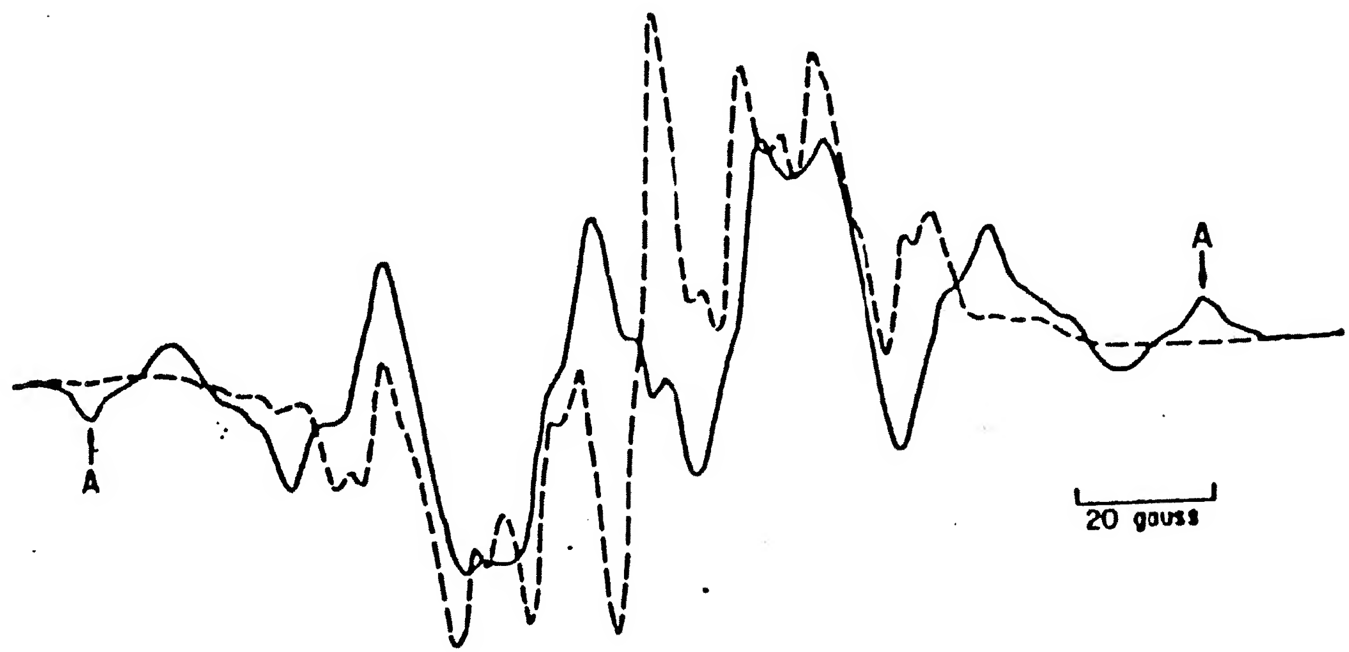


Figure 2. Esr spectra of allyl free radicals (dotted curve) and of mixed alkyl and allyl free radicals after heating to room temperature (solid curve). Decay of alkyl free radicals was calculated from height of peaks marked A.

REFERENCE: D.C. Waterman and M. Dole, J. Phys. Chem., 74 (9), 1970, 1913-1922